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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Bisacylphosphines

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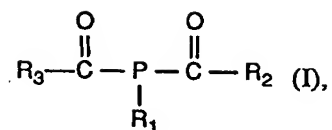
Notice: The specification contained herein as filed

**Canada**

CCA 3254 (10-89) 41

A-18495/ABisacylphosphinesAbstract of the Disclosure

Bisacylphosphines of formula I



wherein  $\text{R}_1$  is unsubstituted  $\text{C}_1\text{-C}_{18}$ alkyl or  $\text{C}_1\text{-C}_8$ alkyl which is substituted by phenyl, -CN,  $\text{C}_1\text{-C}_{12}$ alkoxy or halogen,  $\text{C}_2\text{-C}_{18}$ alkenyl, unsubstituted  $\text{C}_5\text{-C}_8$ cycloalkyl or  $\text{C}_5\text{-C}_8$ cycloalkyl which is substituted by  $\text{C}_1\text{-C}_{12}$ alkyl,  $\text{C}_1\text{-C}_{12}$ alkoxy or halogen, or a 5- or 6-membered aromatic heterocyclic radical which contains oxygen, sulfur and/or nitrogen and is unsubstituted or substituted by halogen,  $\text{C}_1\text{-C}_4$ alkyl or  $\text{C}_1\text{-C}_4$ alkoxy, and  $\text{R}_2$  and  $\text{R}_3$  are each independently of the other unsubstituted  $\text{C}_1\text{-C}_{18}$ alkyl or  $\text{C}_1\text{-C}_8$ alkyl which is substituted by phenyl, halogen or  $\text{C}_1\text{-C}_{12}$ alkoxy,  $\text{C}_2\text{-C}_6$ alkenyl, unsubstituted  $\text{C}_5\text{-C}_8$ cycloalkyl or  $\text{C}_5\text{-C}_8$ cycloalkyl which is substituted by  $\text{C}_1\text{-C}_{12}$ alkyl,  $\text{C}_1\text{-C}_{12}$ alkoxy or halogen, unsubstituted  $\text{C}_6\text{-C}_{12}$ aryl or  $\text{C}_6\text{-C}_{12}$ aryl which is substituted by  $\text{C}_1\text{-C}_{12}$ alkyl,  $\text{C}_1\text{-C}_{12}$ alkoxy,  $\text{C}_2\text{-C}_{12}$ alkoxyalkyl,  $\text{C}_1\text{-C}_4$ alkylthio or halogen, or a 5- or 6-membered aromatic heterocyclic radical which contains oxygen, sulfur and/or nitrogen and is unsubstituted or substituted by halogen,  $\text{C}_1\text{-C}_4$ alkyl or  $\text{C}_1\text{-C}_4$ alkoxy, can be used as photoinitiators for the photopolymerisation of compounds which contain ethylenically unsaturated double bonds.

A-18495/ABisacylphosphines

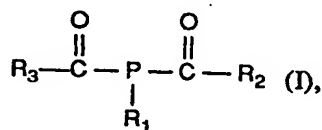
The present invention relates to photocurable compositions which contain bisacylphosphines, to the use of these compounds as initiators for the photopolymerisation of ethylenically unsaturated compounds, and to a process for photopolymerising such compounds with bisacylphosphines as photoinitiators.

Aryl-substituted mono-, bis- and trisacylphosphines have been proposed as photoinitiators in US-A-3 668 093.

Bisacylphosphines are disclosed as educts for the preparation of bisacylphosphine oxide photoinitiators in EP-A-184 095.

It has now been found that bisacylphosphines are also most effective photoinitiators for the polymerisation of compounds containing ethylenically unsaturated double bonds.

Accordingly, the invention relates to photopolymerisable compositions comprising  
(a) at least one ethylenically unsaturated photopolymerisable compound, and  
(b) as photoinitiator, at least one compound of formula I



wherein  $\text{R}_1$  is unsubstituted  $\text{C}_1\text{-C}_{18}$ alkyl or  $\text{C}_1\text{-C}_8$ alkyl which is substituted by phenyl, -CN,  $\text{C}_1\text{-C}_{12}$ alkoxy or halogen,  $\text{C}_2\text{-C}_{18}$ alkenyl, unsubstituted  $\text{C}_5\text{-C}_8$ cycloalkyl or  $\text{C}_5\text{-C}_8$ cycloalkyl which is substituted by  $\text{C}_1\text{-C}_{12}$ alkyl,  $\text{C}_1\text{-C}_{12}$ alkoxy or halogen, or a 5- or 6-membered aromatic heterocyclic radical which contains oxygen, sulfur and/or nitrogen and is unsubstituted or substituted by halogen,  $\text{C}_1\text{-C}_4$ alkyl or  $\text{C}_1\text{-C}_4$ alkoxy, and  $\text{R}_2$  and  $\text{R}_3$  are each independently of the other unsubstituted  $\text{C}_1\text{-C}_{18}$ alkyl or  $\text{C}_1\text{-C}_8$ alkyl which is substituted by phenyl, halogen or  $\text{C}_1\text{-C}_{12}$ alkoxy,  $\text{C}_2\text{-C}_6$ alkenyl, unsubstituted

C<sub>5</sub>-C<sub>8</sub>cycloalkyl or C<sub>5</sub>-C<sub>8</sub>cycloalkyl which is substituted by C<sub>1</sub>-C<sub>12</sub>alkyl, C<sub>1</sub>-C<sub>12</sub>alkoxy or halogen, unsubstituted C<sub>6</sub>-C<sub>12</sub>aryl or C<sub>6</sub>-C<sub>12</sub>aryl which is substituted by C<sub>1</sub>-C<sub>12</sub>alkyl, C<sub>1</sub>-C<sub>12</sub>alkoxy, C<sub>2</sub>-C<sub>12</sub>alkoxyalkyl, C<sub>1</sub>-C<sub>4</sub>alkylthio or halogen, or a 5- or 6-membered aromatic heterocyclic radical which contains oxygen, sulfur and/or nitrogen and is unsubstituted or substituted by halogen, C<sub>1</sub>-C<sub>4</sub>alkyl or C<sub>1</sub>-C<sub>4</sub>alkoxy.

R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> as C<sub>1</sub>-C<sub>18</sub>alkyl may be branched and unbranched alkyl, including methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, pentyl, hexyl, tert-hexyl, heptyl, 2,4,4-trimethylpentyl, octyl, nonyl, decyl, dodecyl, tetradecyl, heptadecyl or octadecyl. R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> may preferably be C<sub>1</sub>-C<sub>12</sub>alkyl.

R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> as C<sub>1</sub>-C<sub>8</sub>alkyl which carries one or more, conveniently one to three and, preferably, one or two, substituents, may be benzyl, 1-phenylethyl, 2-phenylethyl, α,α-dimethylbenzyl, 2-methoxyethyl, 2-ethoxyethyl, diethoxymethyl, 2-butoxyethyl, 2-isopropoxyethyl, 2-butoxypropyl, 2-octyloxyethyl, chloromethyl, 2-chloroethyl or trichloromethyl, and are preferably substituted C<sub>1</sub>-C<sub>4</sub>alkyl, more particularly benzyl. R<sub>1</sub> may also be cyanomethyl, cyanoethyl and the like.

R<sub>1</sub> as C<sub>2</sub>-C<sub>18</sub>alkenyl may be allyl, methallyl, 1,1-dimethylallyl, butenyl, 2-hexenyl, octenyl, undecenyl, dodecenyl or octadecenyl, and is preferably C<sub>2</sub>-C<sub>12</sub>alkenyl, most preferably C<sub>2</sub>-C<sub>6</sub>alkenyl.

R<sub>2</sub> and R<sub>3</sub> as C<sub>2</sub>-C<sub>6</sub>alkenyl may be vinyl, propenyl, butenyl or hexenyl.

R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> as C<sub>5</sub>-C<sub>8</sub>cycloalkyl may be cyclopentyl, cyclohexyl or cyclooctyl, preferably cyclopentyl and cyclohexyl, preferably cyclohexyl. R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> as substituted C<sub>5</sub>-C<sub>8</sub>cycloalkyl, conveniently mono- to tetrasubstituted, C<sub>5</sub>-C<sub>8</sub>cycloalkyl, may be methylcyclopentyl, dimethylcyclopentyl, methylcyclohexyl, dimethylcyclohexyl, diethylcyclohexyl, methoxycyclopentyl, dimethoxycyclopentyl, ethoxycyclopentyl, diethoxycyclopentyl, methoxycyclohexyl, dimethoxycyclohexyl, ethoxycyclohexyl, diethoxycyclohexyl, chlorocyclohexyl, chlorocyclopentyl, dichlorocyclohexyl or dichlorocyclopentyl. Substituted cycloalkyl is preferably C<sub>1</sub>-C<sub>4</sub>alkyl-substituted cycloalkyl.

R<sub>2</sub> and R<sub>3</sub> as C<sub>6</sub>-C<sub>12</sub>aryl may be phenyl, α-naphthyl, β-naphthyl or 4-diphenyl, preferably phenyl. R<sub>2</sub> and R<sub>3</sub> as substituted C<sub>6</sub>-C<sub>12</sub>aryl preferably carry 1 to 3 substituents

and may be chlorophenyl, dichlorophenyl, trichlorophenyl, difluorophenyl, tolyl, mesityl, ethylphenyl, tert-butylphenyl, dodecylphenyl, methoxyphenyl, dimethoxyphenyl, ethoxyphenyl, hexyloxyphenyl, methylnaphthyl, isopropylmethylphenyl, chloronaphthyl, ethoxynaphthyl, methoxyethylphenyl, ethoxymethylphenyl, methylthiophenyl, isopropylthiophenyl or tert-butylthiophenyl, preferably dimethoxyphenyl, chlorophenyl and mesityl, preferably dimethoxyphenyl. Alkyl and alkoxy as substituents of aryl contain 1 to 4 carbon atoms and are preferably methyl or methoxy.

A heterocyclic radical  $R_1$ ,  $R_2$  and  $R_3$  may be mononuclear or polynuclear, preferably mono- or binuclear, typically with a fused benzene ring, and may be furyl, thienyl, pyrrolyl, pyridyl, indolyl, benzoxazolyl, benzimidazolyl or benzthiazolyl. Such a heterocyclic radical preferably contains 4 to 12 carbon atoms. These heterocyclic radicals may carry one or more, conveniently one or two, substituents. Illustrative examples are dimethylpyridyl, methylquinolyl, dimethylpyrrolyl, methoxyfuryl, dimethoxypyridyl or difluoropyridyl.

Halogen is preferably chloro, bromo or fluoro, most preferably chloro.

In preferred compositions,  $R_1$  is unsubstituted  $C_1$ - $C_{12}$ alkyl or  $C_1$ - $C_8$ alkyl which is substituted by phenyl, -CN,  $C_1$ - $C_4$ alkoxy or halogen,  $C_2$ - $C_{12}$ alkenyl, unsubstituted  $C_5$ - $C_8$ cycloalkyl or  $C_5$ - $C_8$ cycloalkyl which is substituted by  $C_1$ - $C_{12}$ alkyl,  $C_1$ - $C_4$ alkoxy or halogen, or a 5- or 6-membered aromatic heterocyclic radical which contains oxygen, sulfur and/or nitrogen and is unsubstituted or substituted by halogen,  $C_1$ - $C_4$ alkyl or  $C_1$ - $C_4$ alkoxy, and  $R_2$  and  $R_3$  are each independently of the other unsubstituted  $C_1$ - $C_{12}$ alkyl or  $C_1$ - $C_8$ alkyl which is substituted by phenyl, halogen or  $C_1$ - $C_4$ alkoxy,  $C_2$ - $C_6$ alkenyl, unsubstituted  $C_5$ - $C_8$ cycloalkyl or  $C_5$ - $C_8$ cycloalkyl which is substituted by  $C_1$ - $C_{12}$ alkyl,  $C_1$ - $C_4$ alkoxy or halogen, unsubstituted  $C_6$ - $C_{12}$ aryl or  $C_6$ - $C_{12}$ aryl which is substituted by  $C_1$ - $C_{12}$ alkyl,  $C_1$ - $C_4$ alkoxy,  $C_2$ - $C_8$ alkoxyalkyl,  $C_1$ - $C_4$ alkylthio or halogen, or a 5- or 6-membered aromatic heterocyclic radical which contains oxygen, sulfur and/or nitrogen and is unsubstituted or substituted by halogen,  $C_1$ - $C_4$ alkyl or  $C_1$ - $C_4$ alkoxy.

Interesting compositions are also those wherein  $R_1$  is unsubstituted  $C_1$ - $C_{12}$ alkyl or  $C_1$ - $C_4$ alkyl which is substituted by phenyl, -CN,  $C_1$ - $C_4$ alkoxy or halogen,  $C_2$ - $C_6$ alkenyl, or unsubstituted  $C_5$ - $C_8$ cycloalkyl or  $C_5$ - $C_8$ cycloalkyl which is substituted by  $C_1$ - $C_{12}$ alkyl,  $C_1$ - $C_4$ alkoxy or halogen, and  $R_2$  and  $R_3$  are each independently of the other unsubstituted  $C_1$ - $C_{12}$ alkyl or  $C_1$ - $C_4$ alkyl which is substituted by phenyl, halogen or  $C_1$ - $C_4$ alkoxy,

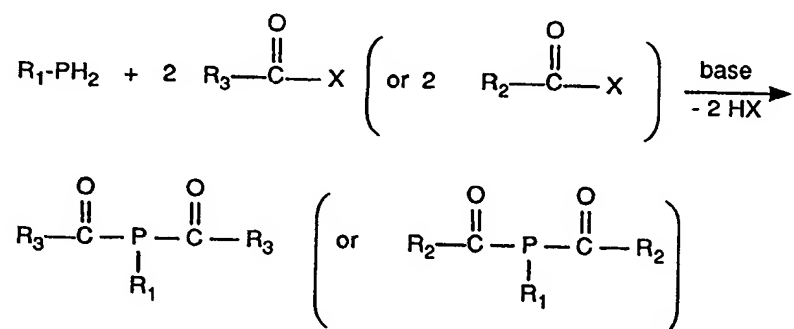
C<sub>2</sub>-C<sub>6</sub>alkenyl, or unsubstituted C<sub>5</sub>-C<sub>8</sub>cycloalkyl or C<sub>5</sub>-C<sub>8</sub>cycloalkyl which is substituted by C<sub>1</sub>-C<sub>12</sub>alkyl, C<sub>1</sub>-C<sub>4</sub>alkoxy or halogen, or unsubstituted C<sub>6</sub>-C<sub>12</sub>aryl or C<sub>6</sub>-C<sub>12</sub>aryl which is substituted by C<sub>1</sub>-C<sub>12</sub>alkyl, C<sub>1</sub>-C<sub>4</sub>alkoxy, C<sub>2</sub>-C<sub>8</sub>alkoxyalkyl, C<sub>1</sub>-C<sub>4</sub>alkylthio or halogen.

Particularly preferred compositions contain compounds of formula I, wherein R<sub>1</sub> is unsubstituted C<sub>1</sub>-C<sub>12</sub>alkyl, phenyl-C<sub>1</sub>-C<sub>4</sub>alkyl, unsubstituted or C<sub>1</sub>-C<sub>12</sub>alkyl-substituted cyclopentyl or cyclohexyl, and R<sub>2</sub> and R<sub>3</sub> are each independently of the other unsubstituted C<sub>1</sub>-C<sub>12</sub>alkyl, phenyl-C<sub>1</sub>-C<sub>4</sub>alkyl, unsubstituted or C<sub>1</sub>-C<sub>12</sub>alkyl-substituted cyclopentyl or cyclohexyl, or unsubstituted phenyl or phenyl which is substituted by C<sub>1</sub>-C<sub>12</sub>alkyl, C<sub>1</sub>-C<sub>4</sub>alkoxy or halogen, most preferably those wherein R<sub>1</sub> is C<sub>1</sub>-C<sub>12</sub>alkyl, cyclohexyl or phenyl-C<sub>1</sub>-C<sub>4</sub>alkyl, and R<sub>2</sub> and R<sub>3</sub> are each independently of the other phenyl which is substituted by C<sub>1</sub>-C<sub>4</sub>alkoxy, halogen or C<sub>1</sub>-C<sub>4</sub>alkyl.

In the compounds of formula I, R<sub>2</sub> and R<sub>3</sub> are preferably identical.

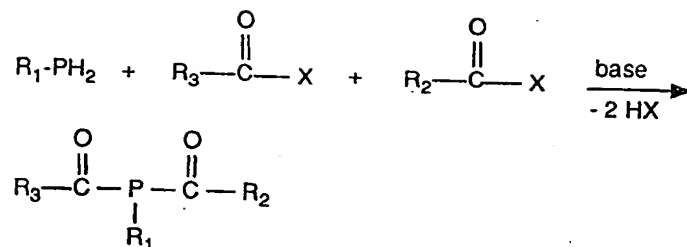
The preparation of the bisacylphosphines is known to those skilled in the art and disclosed in the literature, for example in EP-A-184 095. Thus they may be prepared by reacting a suitable acid halide or a mixture of two acid halides with a primary phosphine, preferably in the approximate stoichiometric ratio of 2:1, in the presence of a base, preferably an amine base, in accordance with reaction schemes [(a)] and [(b)]:

(a)



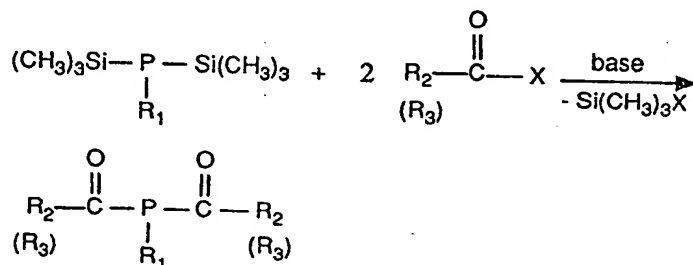
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(b)



The phosphine may also conveniently be bis(trimethylsilyl)phosphine. In the reaction with the acid halide, the trimethylsilyl groups are replaced by the acid radical [(c)]:

(c)



The radicals  $\text{R}_1$ ,  $\text{R}_2$  and  $\text{R}_3$  are as defined in the claim, and X is halogen, preferably chloro.

The preparation of the primary phosphines is known to those skilled in the art, and is described, for example, in Houben-Weyl, Methoden der organischen Chemie, Vol. XII/1, pages 17-79, (1963), Georg Thieme Verlag Stuttgart, and Houben-Weyl, Methoden der organischen Chemie, Vol. E1, pages 106-183, (1982), Georg Thieme Verlag Stuttgart.

The invention further relates to the use of compounds of formula I as photoinitiators for the photopolymerisation of ethylenically unsaturated compounds.

In the practice of this invention, the compounds of formula I can be used as photoinitiators for the photopolymerisation of ethylenically unsaturated compounds or mixtures which contain such compounds. Compound (a) of the compositions of this invention may suitably be selected from ethylenically unsaturated monomers, oligomers and polymers which react by photopolymerisation to form products of high molecular weight and thereby change their solubility.

The unsaturated compounds may contain one or more olefinic double compounds. They may be low molecular weight compounds (monomers) or high molecular weight compounds (oligomers).

Particularly suitable unsaturated compounds include esters of ethylenically unsaturated carboxylic acids and polyols or polyepoxides, and polymers containing ethylenically unsaturated groups in the chain or in side groups, including unsaturated polyesters, polyamides and polyurethanes and copolymers thereof, polybutadiene and butadiene, copolymers, polyisoprene and isoprene copolymers, polymers and copolymers containing (meth)acrylic groups in side-chains, as well as mixtures of one or more such polymers.

Unsaturated carboxylic acids are typically acrylic acid, methacrylic acid, crotonic acid, itaconic acid, cinnamic acid, unsaturated fatty acids, such as linolenic acid or oleic acid. Acrylic acid and methacrylic acid are preferred.

Suitable polyols are aromatic polyols and, preferably, aliphatic and cycloaliphatic polyols. Illustrative examples of aromatic polyols are hydroquinone, 4,4'-dihydroxydiphenyl, 2,2-bis(4-hydroxyphenyl)propane, as well as novolaks and resols. Polyepoxides include those based on the cited polyols, preferably on the aromatic polyols and epichlorohydrin. Further suitable polyols are polymers and copolymers, which contain hydroxyl groups in the polymer chain or in side groups, for example polyvinyl alcohol and copolymers thereof or polymethacrylic hydroxyalkyl esters or copolymers thereof. Other suitable polyols are oligoesters containing hydroxyl end groups.

Illustrative examples of aliphatic and cycloaliphatic polyols are alkylenediols containing preferably 2 to 12 carbon atoms, such as ethylene glycol, 1,2- or 1,3-propanediol, 1,2-, 1,3- or 1,4-butanediol, pentanediol, hexanediol, octanediol, dodecanediol, diethylene glycol, triethylene glycol, polyethylene glycols having molecular weights of preferably 200 to 1500, 1,3-cyclopentanediol, 1,2-, 1,3- or 1,4-cyclohexanediol, 1,4-dihydroxy-methylcyclohexane, glycerol, tris( $\beta$ -hydroxyethyl)amine, trimethylolmethane, trimethylolpropane, pentaerythritol, dipentaerythritol and sorbitol.

The polyols may be esterified partially or completely with one or with different unsaturated carboxylic acids, in which case the free hydroxyl groups of the partial esters may be modified, for example etherified, or esterified with other carboxylic acids.



Illustrative examples of esters are: trimethylolpropane triacrylate, trimethylolethane triacrylate, trimethylolpropane trimethacrylate, trimethylolethane trimethacrylate, tetramethylene glycol dimethacrylate, triethylene glycol dimethacrylate, tetraethylene glycol diacrylate, pentaerythritol diacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, dipentaerythritol diacrylate, dipentaerythritol triacrylate, dipentaerythritol tetraacrylate, dipentaerythritol pentacrylate, dipentaerythritol hexacrylate, tripentaerythritol octacrylate, pentaerythritol dimethacrylate, pentaerythritol trimethacrylate, dipentaerythritol dimethacrylate, dipentaerythritol tetramethacrylate, tripentaerythritol octamethacrylate, pentaerythritol diitaconate, dipentaerythritol trisitaconate, dipentaerythritol pentaitaconate, dipentaerythritol hexaitaconate, ethylene glycol diacrylate, 1,3-butanediol diacrylate, 1,3-butanediol dimethacrylate, 1,4-butanediol diitaconate, sorbitol triacrylate, sorbitol tetraacrylate, pentaerythritol-modified triacrylate, sorbitol tetramethacrylate, sorbitol pentacrylate, sorbitol hexacrylate, oligoester acrylates and methacrylates, glycerol di- and -triacrylate, 1,4-cyclohexanediacylate, bisacrylates and bismethacrylates of polyethylene glycol having molecular weights of 200 to 1500, or mixtures thereof.

Also suitable for use as component (a) are the amides of identical or different unsaturated carboxylic acids of aromatic, cycloaliphatic and aliphatic polyamines containing preferably 2 to 6, more particularly 2 to 4, amino groups. Exemplary of such polyamines are ethylenediamine, 1,2- or 1,3-propylenediamine, 1,2-, 1,3- or 1,4-butylenediamine, 1,5-pentylenediamine, 1,6-hexylenediamine, octylenediamine, dodecylenediamine, 1,4-diaminocyclohexane, isophoronediamine, phenylenediamine, bisphenylenediamine, bis( $\beta$ -aminoethyl) ether, diethylenetriamine, triethylenetetramine, bis( $\beta$ -aminoethoxy)ethane or bis( $\beta$ -aminopropoxy)ethane. Other suitable polyamines are polymers and copolymers which may contain additional amino groups in the side-chain and oligoamides containing amino end groups.

Exemplary of such unsaturated amides are: methylenebisacrylamide, 1,6-hexamethylenebisacrylamide, diethylenetriaminetrimethacrylamide, bis(methacrylamidopropoxy)ethane,  $\beta$ -methacrylamidoethylmethacrylate, N-[( $\beta$ -hydroxyethoxy)ethyl]acrylamide.

Suitable unsaturated polyesters and polyamides are derived typically from maleic acid and diols or diamines. Maleic acid can be partially replaced by other dicarboxylic acids. They can be used together with ethylenically unsaturated comonomers, as with styrene. The

polyesters and polyamides can also be derived from dicarboxylic acids and ethylenically unsaturated diols or diamines, especially from those with long chains containing typically from 6 to 20 carbon atoms. Polyurethanes are typically those derived from saturated or unsaturated diisocyanates and unsaturated and saturated diols.

Polybutadiene and polyisoprene and copolymers thereof are known. Suitable comonomers include olefins such as ethylene, propene, butene, hexene, (meth)acrylates, acrylonitrile, styrene or vinyl chloride. Polymers containing (meth)acrylate groups in the side-chain are also known. They may typically be reaction products of epoxy resins based on novolak with (meth)acrylic acid, homo- or copolymers of polyvinyl alcohol or their hydroxyalkyl derivatives which are esterified with (meth)acrylic acid or homo- and copolymers of (meth)acrylates which are esterified with hydroxyalkyl(meth)acrylates.

The photopolymerisable compounds can be used by themselves or in any desired mixtures. It is preferred to use mixtures of polyol(meth)acrylates.

Binders may also be added to the compositions of the invention. The addition of binders is particularly useful if the photopolymerisable compounds are liquid or viscous substances. The amount of binder may be from 5-95, preferably 10-90 and, most preferably, 50-90, percent by weight, based on the entire composition. The choice of binder will depend on the field of use and the desired properties therefor, such as the ability of the compositions to be developed in aqueous and organic solvent systems, adhesion to substrates and susceptibility to oxygen.

Suitable binders are typically polymers having a molecular weight of about 5000-2 000 000, preferably 10 000-1 000 000. Illustrative examples are: homo- and copolymers of acrylates and methacrylates, including copolymers of methyl methacrylate/ethyl acrylate/methacrylic acid, poly(alkylmethacrylates), poly(alkylacrylates); cellulose esters and ethers such as cellulose acetate, cellulose acetobutyrate, methyl cellulose, ethyl cellulose; polyvinyl butyral, polyvinyl formal, cyclised rubber, polyethers such as polyethylene oxide, polypropylene oxide, polytetrahydrofuran; polystyrene, polycarbonate, polyurethane, chlorinated polyolefins, polyvinyl chloride, copolymers of vinyl chloride/vinylidene chloride, copolymers of vinylidene chloride with acrylonitrile, methyl methacrylate and vinyl acetate, polyvinyl acetate, copoly(ethylene/vinyl acetate), polymers such as polycaprolactam and poly(hexamethylene adipamide), polyesters such as poly(ethylene glycol terephthalate) and

poly(hexamethylene glycol succinate).

The unsaturated compounds can also be used in admixture with non-photopolymerisable film-forming components. These components may be physically drying polymers or solutions thereof in organic solvents, for example nitrocellulose or cellulose acetobutyrate. They may, however, also be chemically or thermally curable resins such as polyisocyanates, polyepoxides or melamine resins. The concurrent use of thermally curable resins is important for the use in so-called hybrid systems which, in a first step, are photopolymerised and, in a second step, crosslinked by a thermal aftertreatment.

The photopolymerisable compositions of this invention conveniently contain the photoinitiator (b) in an amount of 0.05 to 15 % by weight, preferably of 0.2 to 5 % by weight, based on the composition.

The invention also relates to compositions which comprise, in addition to the photoinitiator (b), at least one further photoinitiator and/or other additives.

Further different additives which may be present in the photopolymerisable compositions in addition to the photoinitiator are typically thermal inhibitors which, especially during the preparation of the compositions by mixing the components, prevent premature polymerisation. Such further additives are typically hydroquinone, hydroquinone derivatives, p-methoxyphenol,  $\beta$ -naphthol or sterically hindered phenols, such as 2,6-di(tert-butyl)p-cresol.

To enhance storage stability in the dark it is possible to add copper compounds, including copper naphthenate, copper stearate or copper octoate, phosphorus compounds, including triphenylphosphine, tributylphosphine, triethyl phosphite, triphenyl phosphite, or tribenzyl phosphite, quaternary ammonium compounds, such as tetramethylammonium chloride or trimethylbenzylammonium chloride, or hydroxylamine derivatives, such as N-diethylhydroxylamine.

The exclusion of atmospheric oxygen during the polymerisation may be effected by adding paraffin or similar wax-like substances which, at the onset of polymerisation, migrate to the surface owing to lack of solubility in the polymer and form a transparent film which prevents air from entering the system.

Minor amounts of UV absorbers, typically those of the benzotriazole, benzophenone or oxanilide type, may be added as light stabilisers. Light stabilisers of the sterically hindered amine type (HALS) can also be added.

In specific cases it can be advantageous to use mixtures of two or more photoinitiators of this invention. Further photoinitiators used in addition to the photoinitiators of formula I may be those selected from the following types: benzophenones, acetophenone derivatives, such as  $\alpha$ -hydroxyalkylphenylketones, benzoin alkyl ethers and benzil ketals, or acyl phosphine oxides, bisacylphosphine oxides or titanocenes.

The photopolymerisation can be accelerated, especially in pigmented formulations, by adding amines, such as triethanolamine, N-methyl-diethanolamine, ethyl p-dimethylaminobenzoate or Michler's ketone. The action of the amines can be intensified by the addition of aromatic ketones of the benzophenone type.

The photopolymerisation can further be accelerated by the addition of photosensitisers which shift or broaden the spectral sensitivity. These photosensitisers are preferably aromatic carbonyl compounds such as benzophenone, thioxanthone, anthraquinone and 3-acylcoumarin derivatives as well as 3-(aroylmethylene)thiazolines.

Depending on the envisaged end use, further customary additives are fillers, pigments, dyes, adhesion promoters, wetting agents or levelling agents.

The photopolymerisable compositions can be used for a variety of purposes, including their use in printing ink compositions, in clear coating formulations, in white enamels, in paints, in paints for exterior coatings, and for photographic reproduction processes, for image recording processes or for the production of printing plates, for stereolithography, as dental filling compositions, as adhesives, as coatings for optical fibres, for printed circuits or for coating electronic components.

In coating formulations there are frequently used two-component mixtures of a prepolymer with a polyunsaturated monomer or three-component mixtures which contain an additional mono-unsaturated monomer. The prepolymer primarily determines the properties of the coat and, by varying it, the skilled person can influence the properties of the cured film. The polyunsaturated monomer acts as crosslinker which makes the coating film insoluble. The mono-unsaturated monomer acts as reactive diluent with the aid of

which the viscosity is lowered without having to use a solvent.

Two- and three-component systems based on a prepolymer are used for printing inks as well as for coating compositions, photoresists or other photocurable compositions. Single component systems based on photocurable prepolymers are also often used as binders for printing inks.

Unsaturated polyester resins are normally used together with a mono-unsaturated monomer, preferably with styrene. Specific single component systems are often used for photoresists, for example the polymaleimides, polychalcones or polyimides disclosed in DE-OS 2 308 830.

The photocurable compositions of this invention may suitably be used as coating compositions for substrates of all kinds, such as wood, paper, ceramics, synthetic resins such as polyesters and cellulose acetate films, and metals such as copper and aluminium, to which it is desired to apply a protective layer or an image by photopolymerisation.

The substrate can be coated by applying to said substrate a liquid composition, a solution or suspension. This is done typically by dip-coating, brushing, spraying or reverse roller coating. The add-on (layer thickness) and the nature of the substrate (support) will depend on the desired field of application. Suitable substrates for recording photographic information are sheets of polyester, cellulose acetate or resin-coated papers. Specially treated aluminium is used for offset printing formes, and copper-clad laminates for making printed circuit boards. The layer thicknesses for photographic materials and offset printing formes are normally about 0.5 to about 10  $\mu\text{m}$ . If solvents are concurrently used, these can be removed after coating.

Photocuring is of great importance for printing inks, as the drying time of the binder is a decisive factor in the rate of production of graphic products and should be in the order of fractions of seconds. UV curable printing inks are of particular importance for screen printing.

The photocurable compositions of this invention are also very suitable for making printing plates. For this utility mixtures of soluble linear polyamides or styrene/butadiene rubber with photopolymerisable monomers, typically acrylamides, and a photoinitiator, are used. Films and plates of these systems (wet or dry) are exposed via the negative (or positive) of

the original and the non-cured parts are subsequently eluted with a solvent.

A further field of use of photocuring is metal coating, as in the coating of sheet metal and tubes, cans or bottle caps, as well as the photocuring of resin coatings, for example PVC floor or wall coverings.

Illustrative of the photocuring of paper coatings is the colourless coating of labels, record sleeves or book jackets.

The use of photocurable compositions is also important for imaging techniques and for the optical production of information carriers. For these utilities, the layer (wet or dry) applied to the substrate is irradiated through a photomask with shortwave light and the unexposed areas of the layer are removed by treatment with a solvent (= developer). The application of the photocurable layer can also be effected by electrodeposition on metal. The exposed areas are crosslinked-polymeric and hence insoluble and remain on the substrate. Visible images are formed by appropriate colouration. If the substrate is a metallised layer, then the metal can be etched away after exposure and development at the unexposed areas or reinforced by galvanising. In this manner it is possible to make printed circuit boards and photoresists.

The invention further relates to a process for photopolymerising monomeric, oligomeric or polymeric compounds containing at least one ethylenically unsaturated double bond, which comprises adding to said compounds a compound of formula I and irradiating with light of wavelengths in the range from 200 to 600 nm.

Polymerisation is carried out by known methods of photopolymerisation by irradiation with sunlight or with light which is rich in shortwave radiation. Suitable light sources are typically mercury medium-pressure, high-pressure and low-pressure lamps, superactinic fluorescent tubes, metal halide lamps or lasers the maximum emissions of which are in the range from 250-450 nm. Laser light sources have the advantage that no photomasks are necessary, as the controlled laser beam writes direct onto the photocurable layer. Where combinations with photosensitisers are used, it is also possible to use light of longer wavelength or laser beams of up to 600 nm.

The compositions are conveniently prepared by mixing the individual components.

The invention further relates to a cured composition which is obtained by the above described process.

The bisacylphosphines of this invention have good solubility in the substrates. They are photoinitiators of good reactivity. Substrates which contain the bisacylphosphine photoinitiators exhibit only insignificant yellowing and, in addition, suffer only minor inhibition of polymerisation by atmospheric oxygen.

The invention is described in more detail by the following Examples in which and throughout the remainder of the description and in the claims, parts and percentages are by weight, unless otherwise indicated.

Example 1: Preparation of bis(2,6-dimethoxybenzoyl)-(2-methylpropyl)phosphine

A mixture of 5 ml (0.0425 mol) of (2-methylpropyl)phosphine and 13 ml (0.0935 mol) of triethylamine is added dropwise at 100-110 °C over 30 minutes to 18.8 g (0.0935 mol) of 2,6-dimethoxybenzoyl chloride in 100 ml of toluene. The reaction is brought to completion by stirring the reaction mixture at the same temperature for 6 hours, whereupon the product, as well as triethylammonium chloride, fall out as a yellowish precipitate. After cooling the reaction mixture, the ammonium salt is dissolved by addition of water and the product is isolated by filtration and dried under vacuum, affording 11.1 g (62.5 % of theory) of the title compound in the form of a white powder with a melting point of 138-140 °C.

Elemental analysis:	C calcd:	63.15 %	H calcd:	6.50 %
	found:	63.19 %	found:	6.52 %

Example 2: Preparation of bis(2,6-dichlorobenzoyl)benzylphosphine

A mixture of 39.5 g (0.12 mol) of benzylphosphine (as 38 % solution in toluene) and 37.1 ml (0.266 mol) of triethylamine is added at 100-110 °C over 30 minutes to 38.0 ml (0.266 mol) of 2,6-dichlorobenzoyl chloride in 200 ml of toluene. The reaction is brought to completion by stirring the reaction mixture at the same temperature for 6 hours. The reaction mixture is then diluted with toluene and washed twice with water and dilute hydrogencarbonate solution. The organic phase is dried over magnesium sulfate and concentrated under vacuum. The precipitated reaction product is recrystallised from ethyl acetate, affording 26.8 g (45.5 % of theory) of the title compound in the form of a white

powder with a melting point of 136-137 °C.

Elemental analysis:

C calcd:	53.65%	H calcd:	2.79%	Cl calcd:	30.17%
found:	53.66%	found:	2.85%	found:	30.50 %

Examples 3-5:

The compounds of Examples 3, 4 and 5 are prepared using the appropriate starting primary phosphines in accordance with the general procedure described in Example 1. The compounds and their physical data are reported in Table 1.

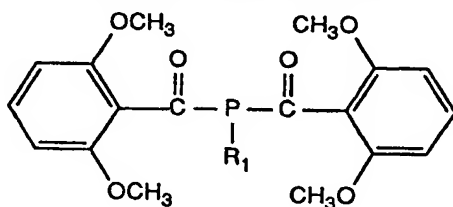


Table 1

Example	R <sub>1</sub>	Melting point [°C]	Elemental analysis [%]		
			C	H	calcd. found
3	$\begin{array}{c} \text{CH}_3 \\   \\ \text{---CH} \\   \\ \text{CH}_2\text{---CH}_3 \end{array}$	121-123	63.15 63.09	6.50 6.37	
4	benzyl	155-157	66.37 66.20	5.57 5.65	
5	n-butyl	113-116	63.15 62.87	6.50 6.80	

Example 6: Preparation of bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine

The compound is prepared using the appropriate starting primary phosphine in accordance with the general procedure described in Example 1. The title compound has a melting point of 114-117°C.



C calcd:	65.81 %	H calcd:	7.43 %
found:	65.70 %	found:	7.59 %

Example 7: Preparation of bis(2,4,6-trimethylbenzoyl)benzylphosphine

62.5 ml (0.10 mol/1.6 M) of butyl lithium are added dropwise over 30 minutes under nitrogen at 0-5 °C to a solution of 14.2 ml (0.10 mol) of diisopropylamine in 25 ml of tetrahydrofuran. This solution is added dropwise at -30 to -40 °C over 90 minutes to a solution of 18.3 g (0.10 mol) of 2,4,6-trimethylbenzoyl chloride and 14.9 g (0.046 mol; 38 % in toluene) of benzyl phosphine in 60 ml of tetrahydrofuran. After stirring for 2 hours at -30°C, the yellow solution is allowed to warm to room temperature and is washed once with water. The organic phase is then dried over magnesium sulfate, filtered and concentrated on a rotary evaporator. The residue is chromatographed (eluant: hexane/ethyl acetate 9:1) and recrystallised from hexane, giving the title compound in the form of a yellow powder with a melting point of 129-130°C.

Elemental analysis:

C calcd:	77.86 %	H calcd:	7.02 %
found:	78.28 %	found:	7.18 %

Example 8: Initiator activity in a white enamel formulation

A photopolymerisable composition comprising the following ingredients is prepared:

- 30 % of <sup>®</sup>Ebecryl 608 (epoxy acrylate, UCB, Belgium)
- 15 % of trimethylolpropane trisacrylate (Degussa)
- 5 % of N-vinylpyrrolidone (Fluka)
- 50 % of titanium dioxide (rutile type; <sup>®</sup>R-TC2 Tioxide, France)

To this composition are added 2 % by weight of the test photoinitiator of Example 1. The formulation is applied in a layer thickness of 100 µm to aluminium sheets and in a layer thickness of 30 µm to glass. The 30 µm layers are then cured in a PPG exposure apparatus by irradiation with mercury medium-pressure lamps (2 x 80 W/cm) and a 120 W/cm Fusion D lamp. The cure is effected by passing the sample under the lamps on a belt moving at a speed of 10 m/min for as often as is necessary to obtain a wipe-resistant coating surface. The fewer the number of passes, the higher the reactivity of the tested compound. The maximum running speed for obtaining the wipe-resistance is determined

for both types of lamp in m/min. (Number of passes [n] at a running speed y [m/min]). The 100  $\mu\text{m}$  layers are cured by irradiation with a Hanovia mercury medium-pressure lamp (80 W/cm). The maximum running speed to effect the full cure in m/min is determined (number of passes [n] at a running speed y [m/min]). The full cure of the sample is determined by means of the pendulum hardness test using the apparatus of König (DIN 53 157). The greater the number of seconds, the harder the tested sample. The yellowing of the sample is determined by measuring the Yellowness Index (YI) in accordance with ASTM D 1925-70. The lower the value, the lesser the yellowing of the sample. The pendulum hardness and the yellowing are determined immediately after the cure and after an additional exposure for 15 minutes and 16 hours under 4 40 W Philips TL 40/03 lamps. The gloss of the sample is measured in accordance with ASTM D 523 at an angle of incidence of 20° and 60° after an additional exposure of 15 minutes and 16 hours. The degree of reflected light is given in %. The higher the values, the better the gloss. The results obtained for the 100  $\mu\text{m}$  layer are summarised in Table 2, and those obtained for the 30  $\mu\text{m}$  layer in Table 3.

Table 2: 100  $\mu\text{m}$  layer

Compound of Example	full cure n x y [m/min]	Pendulum hardness [s]			YI			Gloss 20/60°	
		immed.	15 min	16 h	immed.	15 min	16 h	[in %]	
1	2 x 10	50	98	193	0.8	1.2	1.8	85/92	83/91

Table 3: 30  $\mu\text{m}$  layer

Compound of Example	Wipe resistance n x y [m/min]	
	160 W/cm	120 W/cm
1	2 x 10	2 x 10

#### Example 9: Initiator reactivity in a white enamel formulation

2 % by weight of the photoinitiator of Example 3 is incorporated in a formulation comprising:

- 67.5 % of <sup>®</sup>Ebecryl 830 (polyester acrylate; UCB, Belgium)
- 5.0 % of 1,6-hexanediol diacrylate
- 2.5 % of trimethylolpropane trisacrylate
- 25.0 % of titanium dioxide (rutile; Tioxide, France)

The formulation is applied with a 100  $\mu\text{m}$  draw bar to an aluminium sheet. The layer is cured by irradiation with a 80 W/cm Hanovia mercury medium-pressure lamp. The sample is passed under the lamp on a belt which runs at a speed of 10 m/min. The number of passes is determined which are necessary to effect wipe-resistance of the sample. Immediately after the cure, the Yellowness Index (ASTM D 1925-70) and the pendulum hardness by the method of König (Din 53157) are determined. A post-exposure under 4 Philips TL 40/03 lamps for 15 min. and 16 h is then carried out. The Yellowness Index and the pendulum hardness are again determined after these intervals. The lower the YI value, the lesser the yellowing of the sample. The greater the number of seconds measured during the pendulum hardness test, the harder the tested sample. The results are reported in Table 4.

Table 4: 100  $\mu\text{m}$  layer

Compound of Example	No. of passes at 10 m/min	Pendulum hardness [s]			YI		
		immed.	15 min	16 h	immed.	15 min	16 h
3	4	147	165	189	2.4	1.7	0

Example 10: Initiator reactivity in a clear coating formulation

2 % by weight of the the photoinitiator of Example 1 are incorporated in a formulation comprising

99.5 % of <sup>®</sup>Roskydal UV 502 A (solution of an unsaturated polyester in styrene;  
ex Bayer, FRG) and

0.5 % of <sup>®</sup>Byk 300 (levelling agent, ex Byk-Mallinckrodt)

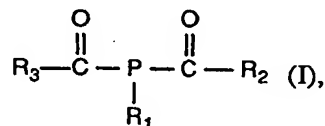
The formulation is applied in a layer thickness of 100  $\mu\text{m}$  to chipboards which are coated with a white synthetic resin. The layer is cured by irradiation in a PPG exposure apparatus with 2 x 80 W/cm mercury medium-pressure lamps. The sample is passed under the source of irradiation on a belt which moves at a speed of 20 m/min. The number of passes necessary to harden the layer until it is wipe-resistant is measured first, followed by the determination of the Yellowness Index (ASTM D 1925-70). The fewer the number of passes, the more reactive the photoinitiator. The lower the YI value, the lesser the yellowing of the sample. The result is reported in Table 5.

Table 5: 100  $\mu\text{m}$  layer

Compound of Example	Full cure n x y [m/min]	Yellowness Index
1	4 x 20	7.4

What is claimed is:

1. A photopolymerisable composition comprising
  - (a) at least one ethylenically unsaturated photopolymerisable compound, and
  - (b) as photoinitiator, at least one compound of formula I



wherein  $\text{R}_1$  is unsubstituted  $\text{C}_1$ - $\text{C}_{18}$ alkyl or  $\text{C}_1$ - $\text{C}_8$ alkyl which is substituted by phenyl, -CN,  $\text{C}_1$ - $\text{C}_{12}$ alkoxy or halogen,  $\text{C}_2$ - $\text{C}_{18}$ alkenyl, unsubstituted  $\text{C}_5$ - $\text{C}_8$ cycloalkyl or  $\text{C}_5$ - $\text{C}_8$ cycloalkyl which is substituted by  $\text{C}_1$ - $\text{C}_{12}$ alkyl,  $\text{C}_1$ - $\text{C}_{12}$ alkoxy or halogen, or a 5- or 6-membered aromatic heterocyclic radical which contains oxygen, sulfur and/or nitrogen and is unsubstituted or substituted by halogen,  $\text{C}_1$ - $\text{C}_4$ alkyl or  $\text{C}_1$ - $\text{C}_4$ alkoxy, and  $\text{R}_2$  and  $\text{R}_3$  are each independently of the other unsubstituted  $\text{C}_1$ - $\text{C}_{18}$ alkyl or  $\text{C}_1$ - $\text{C}_8$ alkyl which is substituted by phenyl, halogen or  $\text{C}_1$ - $\text{C}_{12}$ alkoxy,  $\text{C}_2$ - $\text{C}_6$ alkenyl, unsubstituted  $\text{C}_5$ - $\text{C}_8$ cycloalkyl or  $\text{C}_5$ - $\text{C}_8$ cycloalkyl which is substituted by  $\text{C}_1$ - $\text{C}_{12}$ alkyl,  $\text{C}_1$ - $\text{C}_{12}$ alkoxy or halogen, unsubstituted  $\text{C}_6$ - $\text{C}_{12}$ aryl or  $\text{C}_6$ - $\text{C}_{12}$ aryl which is substituted by  $\text{C}_1$ - $\text{C}_{12}$ alkyl,  $\text{C}_1$ - $\text{C}_{12}$ alkoxy,  $\text{C}_2$ - $\text{C}_{12}$ alkoxyalkyl,  $\text{C}_1$ - $\text{C}_4$ alkylthio or halogen, or a 5- or 6-membered aromatic heterocyclic radical which contains oxygen, sulfur and/or nitrogen and is unsubstituted or substituted by halogen,  $\text{C}_1$ - $\text{C}_4$ alkyl or  $\text{C}_1$ - $\text{C}_4$ alkoxy.

2. A composition according to claim 1, wherein  $\text{R}_1$  is unsubstituted  $\text{C}_1$ - $\text{C}_{12}$ alkyl or  $\text{C}_1$ - $\text{C}_8$ alkyl which is substituted by phenyl, -CN,  $\text{C}_1$ - $\text{C}_4$ alkoxy or halogen,  $\text{C}_2$ - $\text{C}_{12}$ alkenyl, unsubstituted  $\text{C}_5$ - $\text{C}_8$ cycloalkyl or  $\text{C}_5$ - $\text{C}_8$ cycloalkyl which is substituted by  $\text{C}_1$ - $\text{C}_{12}$ alkyl,  $\text{C}_1$ - $\text{C}_4$ alkoxy or halogen, or a 5- or 6-membered aromatic heterocyclic radical which contains oxygen, sulfur and/or nitrogen and is unsubstituted or substituted by halogen,  $\text{C}_1$ - $\text{C}_4$ alkyl or  $\text{C}_1$ - $\text{C}_4$ alkoxy, and  $\text{R}_2$  and  $\text{R}_3$  are each independently of the other unsubstituted  $\text{C}_1$ - $\text{C}_{12}$ alkyl or  $\text{C}_1$ - $\text{C}_8$ alkyl which is substituted by phenyl, halogen or  $\text{C}_1$ - $\text{C}_4$ alkoxy,  $\text{C}_2$ - $\text{C}_6$ alkenyl, unsubstituted  $\text{C}_5$ - $\text{C}_8$ cycloalkyl or  $\text{C}_5$ - $\text{C}_8$ cycloalkyl which is substituted by  $\text{C}_1$ - $\text{C}_{12}$ alkyl,  $\text{C}_1$ - $\text{C}_4$ alkoxy or halogen, unsubstituted  $\text{C}_6$ - $\text{C}_{12}$ aryl or  $\text{C}_6$ - $\text{C}_{12}$ aryl which is substituted by  $\text{C}_1$ - $\text{C}_{12}$ alkyl,  $\text{C}_1$ - $\text{C}_4$ alkoxy,  $\text{C}_2$ - $\text{C}_8$ alkoxyalkyl,  $\text{C}_1$ - $\text{C}_4$ alkylthio or halogen, or a 5- or 6-membered aromatic heterocyclic radical which

contains oxygen, sulfur and/or nitrogen and is unsubstituted or substituted by halogen, C<sub>1</sub>-C<sub>4</sub>alkyl or C<sub>1</sub>-C<sub>4</sub>alkoxy.

3. A composition according to claim 2, wherein R<sub>1</sub> is unsubstituted C<sub>1</sub>-C<sub>12</sub>alkyl or C<sub>1</sub>-C<sub>4</sub>alkyl which is substituted by phenyl, -CN, C<sub>1</sub>-C<sub>4</sub>alkoxy or halogen, C<sub>2</sub>-C<sub>6</sub>alkenyl, or unsubstituted C<sub>5</sub>-C<sub>8</sub>cycloalkyl or C<sub>5</sub>-C<sub>8</sub>cycloalkyl which is substituted by C<sub>1</sub>-C<sub>12</sub>alkyl, C<sub>1</sub>-C<sub>4</sub>alkoxy or halogen, and R<sub>2</sub> and R<sub>3</sub> are each independently of the other unsubstituted C<sub>1</sub>-C<sub>12</sub>alkyl or C<sub>1</sub>-C<sub>4</sub>alkyl which is substituted by phenyl, halogen or C<sub>1</sub>-C<sub>4</sub>alkoxy, C<sub>2</sub>-C<sub>6</sub>alkenyl, or unsubstituted C<sub>5</sub>-C<sub>8</sub>cycloalkyl or C<sub>5</sub>-C<sub>8</sub>cycloalkyl which is substituted by C<sub>1</sub>-C<sub>12</sub>alkyl, C<sub>1</sub>-C<sub>4</sub>alkoxy or halogen, or unsubstituted C<sub>6</sub>-C<sub>12</sub>aryl or C<sub>6</sub>-C<sub>12</sub>aryl which is substituted by C<sub>1</sub>-C<sub>12</sub>alkyl, C<sub>1</sub>-C<sub>4</sub>alkoxy, C<sub>2</sub>-C<sub>8</sub>alkoxyalkyl, C<sub>1</sub>-C<sub>4</sub>alkylthio or halogen.
4. A composition according to claim 3, wherein R<sub>1</sub> is unsubstituted C<sub>1</sub>-C<sub>12</sub>alkyl, phenyl-C<sub>1</sub>-C<sub>4</sub>alkyl, unsubstituted or C<sub>1</sub>-C<sub>12</sub>alkyl-substituted cyclopentyl or cyclohexyl, and R<sub>2</sub> and R<sub>3</sub> are each independently of the other unsubstituted C<sub>1</sub>-C<sub>12</sub>alkyl, phenyl-C<sub>1</sub>-C<sub>4</sub>alkyl, unsubstituted or C<sub>1</sub>-C<sub>12</sub>alkyl-substituted cyclopentyl or cyclohexyl, or unsubstituted phenyl or phenyl which is substituted by C<sub>1</sub>-C<sub>12</sub>alkyl, C<sub>1</sub>-C<sub>4</sub>alkoxy or halogen.
5. A composition according to claim 4, wherein R<sub>1</sub> is C<sub>1</sub>-C<sub>12</sub>alkyl, cyclohexyl or phenyl-C<sub>1</sub>-C<sub>4</sub>alkyl, and R<sub>2</sub> and R<sub>3</sub> are each independently of the other phenyl which is substituted by C<sub>1</sub>-C<sub>4</sub>alkoxy, halogen or C<sub>1</sub>-C<sub>4</sub>alkyl.
6. A composition according to any one of claims 1 to 5, wherein R<sub>2</sub> and R<sub>3</sub> are identical.
7. A composition according to claim 1 which, in addition to the photoinitiator (b), comprises at least one further photoinitiator and/or other additives.
8. A composition according to claim 1 comprising 0.05 to 15 % by weight of component b), based on said composition.
9. A composition according to claim 8 comprising 0.2 to 5 % by weight, of component b), based on said composition.
10. A process for photopolymerising compounds containing ethylenically unsaturated double bonds, which comprises irradiating a composition as claimed in claim 1 with light

in the range from 200 to 600 nm.

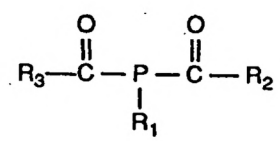
11. A cured composition obtained by the process as claimed in claim 10.

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***REMPLACEMENT***

**SECTION is not Present**  
***Cette Section est Absente***





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